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(54) Title: ION CONDUCTIVE BLOCK COPOLYMERS

(57) Abstract: This invention relates to ion conductive copolymers which are useful in forming polymer electrolyte membranes used in fuel cells.

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## ION CONDUCTIVE BLOCK COPOLYMERS

### TECHNICAL FIELD

This invention relates to ion conductive polymers which are useful in forming polymer electrolyte membranes used in fuel cells.

### 5 BACKGROUND OF THE INVENTION

Fuel cells have been projected as promising power sources for portable electronic devices, electric vehicles, and other applications due mainly to their non-polluting nature. Of various fuel cell systems, the polymer electrolyte membrane based fuel cell technology such as direct methanol fuel cells  
10 (DMFCs) have attracted much interest thanks to their high power density and high energy conversion efficiency. The "heart" of a polymer electrolyte membrane based fuel cell is the so called "membrane-electrode assembly" (MEA), which comprises a proton conducting polymer electrolyte membrane (PEM) catalyst disposed on the opposite surfaces of the PEM to form a  
15 catalyst coated membrane (CCM) and a pair of electrodes (*i.e.*, an anode and a cathode) disposed to be in electrical contact with the catalyst layer.

Proton-conducting membranes for DMFCs are known, such as Nafion® from the E.I. Dupont De Nemours and Company or analogous products from Dow Chemicals. These perfluorinated hydrocarbon sulfonate ionomer products,  
20 however, have serious limitations when used in high temperature fuel cell application Nafion® loses conductivity when the operation temperature of the

fuel cell is over 80°C. Moreover, Nafion® has a very high methanol crossover rate, which impedes its applications in DMFCs.

U.S. Patent No. 5,773,480, assigned to Ballard Power System, describes a partially fluorinated proton conducting membrane from  $\alpha$ ,  $\beta$ ,  $\beta$ -trifluorostyrene. One disadvantage of this membrane is its high cost of manufacturing due to the complex synthetic processes for monomer  $\alpha$ ,  $\beta$ ,  $\beta$ -trifluorostyrene and the poor sulfonation ability of poly ( $\alpha$ ,  $\beta$ ,  $\beta$ -trifluorostyrene). Another disadvantage of this membrane is that it is very brittle, thus has to be incorporated into a supporting matrix.

U.S. Patent Nos. 6,300,381 and 6,194,474 to Kerres, et al. describe an acid-base binary polymer blend system for proton conducting membranes, wherein the sulfonated poly(ether sulfone) was made by post-sulfonation of the poly(ether sulfone).

M. Ueda in the Journal of Polymer Science, 31(1993): 853, discloses the use of sulfonated monomers to prepare the sulfonated poly(ether sulfone) polymers).

U.S. Patent Application US 2002/0091225A1 to McGrath, et al. used this method to prepare sulfonated polysulfone polymers.

The need for a good membrane for fuel cell operation requires balancing of various properties of the membrane. Such properties included proton conductivity, methanol-resistance, chemical stability and methanol crossover especially for high temperature applications, fast start up of DMFCs, and durability of cell performance. In addition, it is important for the membrane to retain its dimensional stability over the fuel operational temperature range. In the case of a DMFC, methanol oxidation generates enough heat to raise the cell temperature. If the membrane swells significantly, it will increase methanol crossover. The membrane thus gradually loses its ability to block methanol crossover, resulting in degradation of cell performance. The dimension changes of the membrane also put a stress on the bonding of the

membrane-electrode assembly (MEA). Often this results in delamination of the membrane from the electrode after excessive swelling of the membrane. Therefore, maintaining the dimensional stability over a wide temperature range and avoiding excessive membrane swelling are important for DMFC applications.

## SUMMARY OF THE INVENTION

The invention provides ion conductive copolymer compositions which can be used to fabricate polymer electrolyte membranes (PEM's), catalyst coated polymer electrolyte membranes (CCM's) and membrane electrode assemblies (MEA's) which are useful in fuel cells.

The ion conductive block copolymer comprises a non-ionic polymer and an ionic polymer covalently linked either directly or indirectly to each other. At least one of the ionic or non-ionic polymers comprises a block polymer in the ion conductive copolymer. Preferably both the ionic and non-ionic polymers are block polymers. The non-ionic polymer comprises two non-ionic comonomers. The ionic polymer comprises two comonomers where at least one comonomer comprises an ion conducting group such as sulfonic acid. In a preferred embodiment, the ionic and non-ionic monomers are reacted separately to produce ionic and/or non-ionic blocks which may thereafter be combined.

The variability of the components of the ion conducting block copolymer provide for the formation of a variety of ion conducting block copolymers. Mixing and matching of these different ionic and non-ionic polymers provides for the formation of the ion conducting block copolymers of the invention. For example, by adjusting the block size, the overall molecular length, the rigidity and the affinity among the ion conducting copolymers, it is possible to control ion channel size distributions and affinity as well fuel cross-over, stability, solubility and mechanical properties of the ion conductive polymer and the membranes made therefrom.

In addition to the foregoing, additional random ionic and/or non-ionic polymers may be interspersed between and among the various non-ionic and ionic blocks of the ion conducting polymer.

## DETAILED DESCRIPTION

5 The invention provides ion conductive block copolymers comprising ionic and non-ionic polymers where one or both of the polymers is a block in the copolymer. The invention also provides polymers which are random in length and/or composition which can be covalently interdispersed between or among the ionic and non-ionic polymers of the ion conductive block copolymer. One  
10 use of such polymeric materials is in the formation of polymer electrolyte membranes (PEMs), catalyst coated membranes (CCM's) and membrane electrolyte assemblies (MEA's) which may be used in direct methanol fuel cells (DMFCs), and the like.

In a preferred embodiment, the ion conductive block copolymer comprises a  
15 non-ionic block comprising monomers made of two non-ionic comonomers and an ionic block comprising an ionic monomer made of two comonomers wherein at least one comonomer comprises an ion conducting group. In general, the ion conductive polymers contain aromatic residues. The ion conductive polymer additionally has groups which facilitate the transport of  
20 ions such as  $H^+$  within and through the copolymer composition.

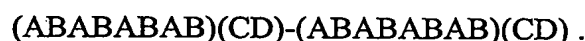
The ion conductive block copolymer in one embodiment can be represented by the following formula:



AB represents a non-ionic monomer made of two different non-ionic  
25 comonomers A and B. AB is combined with other AB's to form the non-ionic polymer  $(AB)_n$ . CD represents an ionic monomer made of two different comonomers C and D at least one of which contains an ion conducting group discussed in more detail below. CD is combined with other CD's to form

ionic polymer  $(CD)_o$ . At least one and preferably both of the  $(AB)_n$  polymer and  $(CD)_o$  polymer are blocks. These ionic and non-ionic polymer are then combined in appropriate proportions to form an ion conducting block copolymer. These units may be combined  $j-1$  times. In the above formula,  
 5 "n" is an integer between 0 and 100, more preferably between 1 and 100 and o is an integer between 1 and 100. More preferably, each of n and o are independently between 1 and 50, more preferably between 5 and 50, still more preferably between 2 and 12. J is an integer between 1 and 200. More preferably between 50 and 150, still more preferably between 100 and 120.  
 10 The ratio of o divided by  $n+o$ , is between .001 and 1, more preferably between 0.15 and 0.7, still more preferably between 0.20 and 0.50.

For example, if  $n = 4$ ,  $o = 1$  and  $j = 2$ , the polymer has the following structure:



The region containing AB is the non-ionic region (block) whereas the region  
 15 containing CD is the ionic region (block).

In general, the non-ionic polymer  $(AB)_n$  is formed by combining chemically reactive precursors to A and B under conditions which allow for the formation of  $(AB)_n$ . However, in some embodiments, it may be desirable to have different A's and/or B's within the non-ionic region. The non-ionic polymer  
 20 may then be represented as  $(A_a B_b)_n$  where a and b represent the number of different A's and B's and are independently between 1 and n the number of  $(A_a B_b)$  units. In this embodiment, the precursors to the different A's and/or B's can be combined to provide for predetermined positioning in the polymer block and/or a random distribution of the different A's and/or B's within  
 25  $(A_a B_b)_n$ . For example, if  $n = 3$  and  $a = 2$  where the amount of  $A_1$  is twice the amount of  $A_2$  in a given polymer and the position of  $A_2$  is at the third position, then the non-ionic block can be represented as a mixture of  $A_1BA_1BA_2B$ .

The ionic polymer comprising  $(CD)_o$  similarly may have the same or different C and/or D, each of which is located at a predetermined or random position in the ionic polymer. The formula representing the ionic region is represented by  $(C_cD_d)_o$  where c and d represent the number of different C's and D's and are  
 5 between 1 and o the number of  $(C_cD_d)$  units.

In addition to the foregoing, the ion conducting copolymers can be represented by the formula:

$$(2) \quad [(A_aB_b)_n(A_gB_h)_m(C_cD_d)_o(C_eD_f)_p]_j.$$

In this formula  $(A_aB_b)_n$  and  $(C_cD_d)_o$  and A, B, C and D are the same as above and  $(A_gB_h)_m$  and  $(C_eD_f)_p$  are polymers which are random in length and/or  
 10 composition. For the random polymers, m and p are numbers between 0 and 200, more preferably between 1 and 20 which define the length of unit  $(A_gB_h)_h$  and  $(C_eD_f)$ , respectively. g and h are numbers between 0 and m and e and f are numbers between 0 and p. When m is a random number between 1 and m  
 15 and/or p is a random number between 1 and p the ion conducting compositions comprise non-ionic and/or ionic random polymer components with different lengths. For example in the non-ionic region, if a=2, b=1, n=3 and m=4, A<sub>1</sub> and A<sub>2</sub> are in predetermined positions in  $(A_aB_b)_n-(A_gB_h)_n$  the mixture copolymers can be represented as being made up of the following:

20  $(A_1BA_1BA_2B)(AB)$   
 $(A_1BA_1BA_2B)(ABAB)$   
 $(A_1BA_1BA_2B)(ABABAB)$   
 $(A_1BA_1BA_2B)(ABABABAB)$ .

Similarly, when c=2, o=3, p=3 and C<sub>1</sub> and C<sub>2</sub> are at predetermined positions in  
 25  $(C_cD_d)_o-(C_eD_f)_p$  the mixture of copolymer can be represented as follows:

$(C_1DC_1DC_2D)(CD)$   
 $(C_1DC_1DC_2D)(CDCD)$



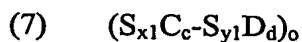
Accordingly, block ionic and/or block non-ionic polymers can be combined with polymers with varying tail lengths to form a mixture of distinct ion conducting partial block copolymers. Alternatively, the tail length of the random polymer components can be random among different molecules or random within a particular copolymer.

When there are more than one type of A, B, C and/or D within the random polymers, such different monomers can be in a predetermined position if the length of the random polymer varies or alternatively randomly distributed over the random polymer. For example, if  $g=2$ ,  $h=1$  and  $n=3$ , the random polymer interposed in formula (2) between the non-ionic and/or ionic blocks can be represented as follows:

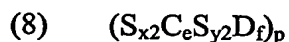


In addition, the polymer may be random both in the position of the different monomers in combination with variation in the length of the random polymer.

The distribution of ion conducting groups in formula (2) can be represented by the following formulas:



alone or in combination with:



where S is an ion conducting group covalently attached to  $C_c$ ,  $D_d$ ,  $C_e$  and/or  $D_f$ .  $X_1$  is the percentage of  $C_c$  which contain S,  $X_2$  is the percentage of  $C_e$  that contains S,  $Y_1$  is the percentage of  $D_d$  which contains S and  $Y_2$  is the percentage of  $D_f$  which contains S where  $(X=X_1 + X_2)$ ,  $(Y=X_1 + Y_2)$  and  $X +$



Y is the total percentage of the C + D units which contain S. At least one of X<sub>1</sub>, X<sub>2</sub>, Y<sub>1</sub> and Y<sub>2</sub> must be greater than zero.

Once made, the ionic and/or non-ionic block and optionally random ionic and/or non-ionic polymers are covalently combined to form a block copolymer having at least ionic and/or non-ionic blocks. This polymer may then be combined with itself j - 1 times. If different ionic conducting block copolymers are used, they may be combined in a random or in a predetermined pattern or both.

The preparation of the disclosed ionic and non-ionic block and random polymers provides flexibility in the formulation of the ion conductive block copolymer. Mixtures of selected component polymers can be combined in defined ratios to provide copolymers having a variety of physical and chemical properties.

In addition to the foregoing, the composition may be slightly modified depending upon how the various polymers making up the composition are made. For example, if precursor for A is in excess to the precursor for B an additional A will be present in the. Similarly, if excess precursor to B is used, there will be an additional B in the same polymer. Similarly, the ion polymer can have an additional D and/or C depending on how the composition is made. Finally, at the juncture of the ionic and non-ionic components, excess A excess B may be present excess B. If, however, approximately molar equivalents are used, the composition will be primarily held in place by covalent bonds rather than additional monomer.

Accordingly, the invention can be defined by the combined formula:

$$(9) \quad \{ -[L_1-(A_aB_b)_n-L_1(A_eB_f)_m]_{1-z} L_2 - [(S_{x1}C_c-S_{y1}D_d)_o-L_3-(S_{x2}C_g-S_{y2}D_h)_p L_3]_z \}_j$$

where  $-[L_1-(A_aB_b)_n-L_1(A_eB_f)_m]_{1-z}$  comprises a non-ionic hydrophobic region,  $[(S_{x1}C_c-S_{y1}D_d)_o-L_3-(S_{x2}C_g-S_{y2}D_h)_p L_3]_z$  comprises an ionic hydrophilic region where

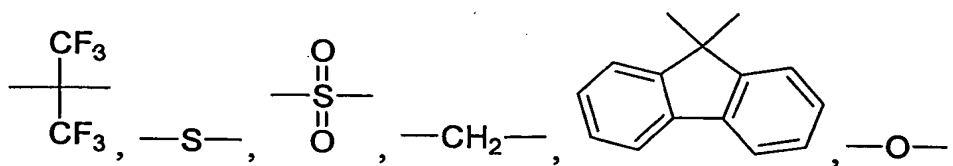
each of the terms are defined as above,  $L_1$  is a bond or an additional A and/or B,  $L_2$  is a bond, or an additional A and/or D, and  $L_3$  is a bond or an additional C and/or D.

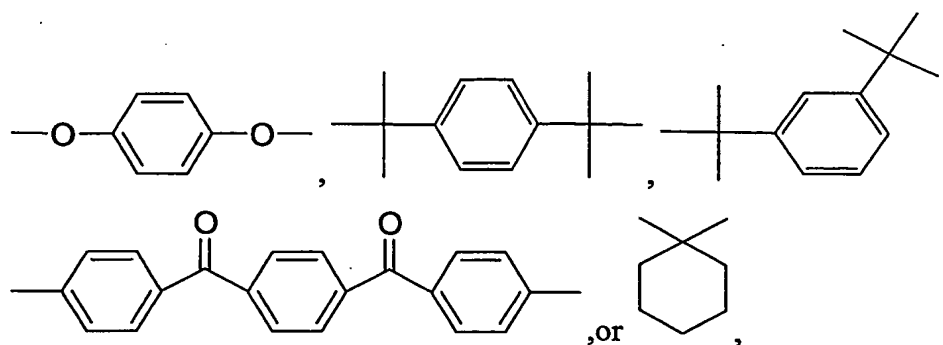
Although A and C can be any hydrophobic residue, it is preferred that A and C contain aromatic groups or substituted aromatic groups. Such substitutions are preferably with one or more electron withdrawing groups, most preferably fluorine.

Particularly preferred A and C residues are phenyl, naphthyl, terphenyl, aryl nitrile, substituted aryl nitrile, organopolysiloxane-- $Ar_1-R_1-Ar_2$ --, where  $R_1$  is,  $-C(O)-$ ,  $-S(O)_2-$ ,  $-P(O)(C_6H_5)-$ ,  $-C(O)-Ar_3-C(O)-$ , or  $-C(O)-Ar_4-S(O)_2-$ , and  $Ar_1$ ,  $Ar_2$ ,  $Ar_3$ , and  $Ar_4$  are aromatic groups and substituted aromatic groups. Such substitutions are preferably with one or more electron withdrawing groups, most preferably with F.

B and D also preferably contain aromatic groups or substituted aromatic groups. Such substitutions are preferably with one or more electron withdrawing groups, most preferably with F. Particularly preferred B and D are:

-- $O-Ar_5-R_2-Ar_6-O$ --, where  $R_2$  is a single bond, cycloaliphatics of the formula  $C_nH_{2n-2}$ ,





and Ar<sub>5</sub> and Ar<sub>6</sub> are aromatic groups or substituted aromatic groups.

Preferred embodiments have the formula:

$$(10) \quad [([Ar_1-R_1-Ar_2-O-Ar_5-R_2-Ar_6-O]_n)([S_{x1}-Ar_1-R_1-S_{y1}-OS_{y5}-Ar_5-R_2-S_{y2}-Ar_6-O]_o)]_z;$$

where each of the components are as defined above. When different components of Ar<sub>1</sub>, R<sub>1</sub>, Ar<sub>2</sub>, Ar<sub>5</sub>, R<sub>2</sub>, and/or Ar<sub>6</sub> are present within the non-ionic and ionic polymer, the distribution of the different components within at least one of the ionic and non-ionic polymers and preferably both can be ordered so as to position the different components at predetermined positions to form one or more blocks in the copolymer.

General methods for the preparation of ion conducting block copolymers are as follows. The methods include the steps of combining a first comonomer with a second comonomer. The first comonomer should have at least two leaving groups and the second comonomer should have at least two displacing groups. In one aspect, the second comonomer is in a molar excess relative to the first comonomer, thereby forming a first copolymer with displacing groups on the end of the first copolymer.

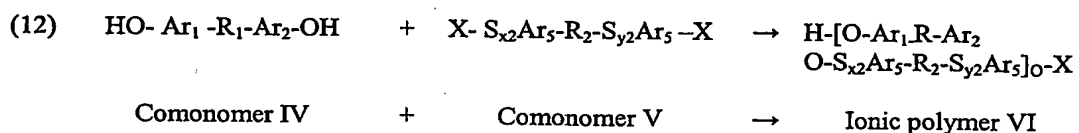
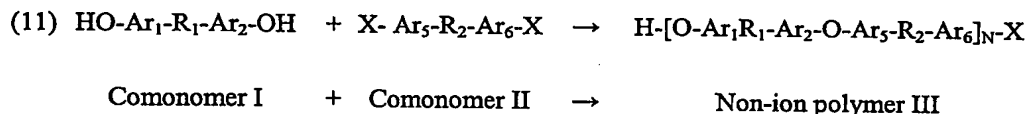
A third comonomer that should have at least two leaving groups and a fourth comonomer that should have at least two displacing groups are then combined. The third comonomer preferably is in molar excess relative to the fourth comonomer, thereby forming a second copolymer having leaving groups on the end of the second copolymer.

The first copolymer is combined with the second copolymer (or vice versa), thereby forming the block copolymer. At least one of the first comonomer or the third comonomer includes an ion conducting group such as a sulfonate group.

5 The term "leaving group" is intended to include those functional moieties that can be displaced by a nucleophilic moiety found, typically, in another monomer. Leaving groups are well recognized in the art and include, for example, halides (chloride, fluoride, iodide, bromide), tosyl, mesyl, etc. In  
10 certain embodiments, the monomer has at least two leaving groups, which are "para" to each other with respect to the aromatic monomer to which they are attached.

The term "displacing group" is intended to include those functional moieties that can act typically as nucleophiles, thereby displacing a leaving group from a suitable monomer. The result is that the monomer to which the displacing  
15 group is attached becomes attached, generally covalently, to the monomer to which the leaving group was associated with. An example of this is the displacement of fluoride groups from aromatic monomers by phenoxide or alkoxide ions associated with aromatic monomers.

20 An example of the synthesis of a non-ionic block and ionic block is set forth in formulas (11) and (12) where X is a leaving group and OH is a displacement group.

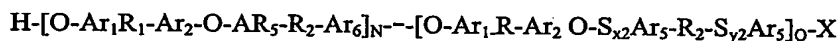
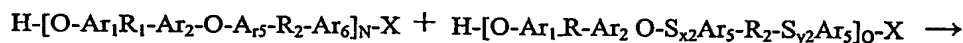


Comonomer I contains two displacement groups (-OH) and comonomer II containing two leaving group (X). The product of the reaction between comonomer I and comonomer II is non-ionic polymer III.

In a separate reaction vessel, monomer IV containing two displacement groups and monomer V containing two leaving groups are combined to produce the ionic polymer VI as shown in formula (12). In each case, the length of the non-ionic and ionic polymers is controlled by reaction conditions including the time, temperature and concentration of the reactants.

Non-ionic polymer III and ionic polymer VI are combined in a reaction vessel to form the ion conducting copolymer VII.

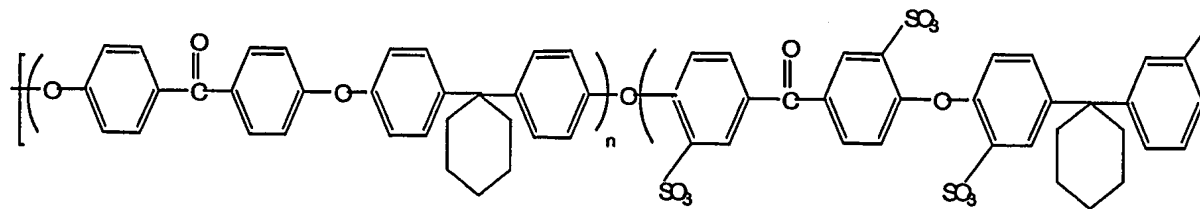
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VII

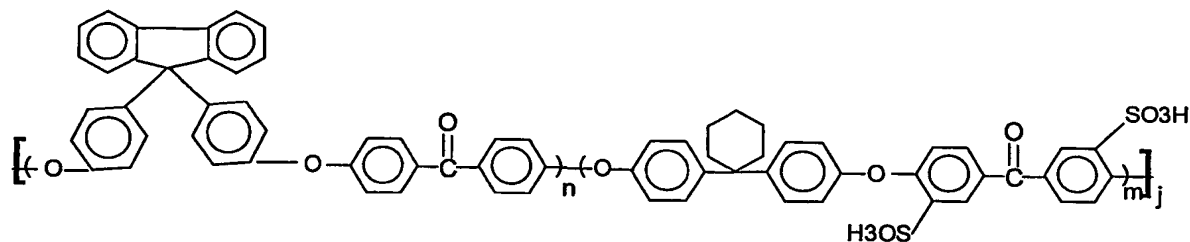
The copolymer can be combined j-1 times.

In a particular preferred embodiment, R<sub>1</sub> is -(CO)-, R<sub>2</sub> is cyclohexydy and S is SO<sub>3</sub>. This is represented by Formula VIII.



where n = 2 - 20; o = 2 - 20; j=1-200. The four sulfonation sites may or may not contain an SO<sub>3</sub> group. However, the total degree of sulfonation is between 10% and 80%.

In another preferred embodiment,  $R_1$  is  $-(CO)-$ ,  $R_2$  is bis and S is  $SO_3$ . This is represented by Formula VIII.



5 where  $n = 220$ ;  $m = 2-20$ ;  $j = 1-100$ . The four sulfonation sites may or may not contain an  $SO_3$  group. However, the total degree of sulfonation is between 10% and 80%.

### VIII

10 Polymer membranes may be fabricated by solution casting of the ion conductive copolymer. Alternatively, the polymer membrane may be fabricated by solution casting the ion conducting polymer the blend of the acid and basic polymer.

15 When cast into a membrane for use in a fuel cell, it is preferred that the membrane thickness be between 0.1 to 10 mils, more preferably between 1 and 6 mils, most preferably between 1.5 and 2.5 mils, and it can be coated over polymer substrate

20 As used herein, a membrane is permeable to protons if the proton flux is greater than approximately 0.005 S/cm, more preferably greater than 0.01 S/cm, most preferably greater than 0.02 S/cm.

As used herein, a membrane is substantially impermeable to methanol if the methanol transport across a membrane having a given thickness is less than the transfer of methanol across a Nafion membrane of the same thickness. In preferred embodiments the permeability of methanol is preferably 50% less

than that of a Nafion membrane, more preferably 75% less and most preferably greater than 80% less as compared to the Nafion membrane.

After the ion conducting copolymer has been formed into a membrane, it may be used to produce a catalyst coated membrane (CCM). As used herein, a CCM comprises a PEM when at least one side and preferably both of the opposing sides of the PEM are partially or completely coated with catalyst. The catalyst is preferable a layer made of catalyst and ionomer. Preferred catalysts are Pt and Pt-Ru. Preferred ionomers include Nafion and other ion conductive polymers. In general, anode and cathode catalysts are applied onto the membrane by well established standard techniques. For direct methanol fuel cells, platinum/ruthenium catalyst is typically used on the anode side while platinum catalyst is applied on the cathode side. For hydrogen/air or hydrogen/oxygen fuel cells platinum or platinum/ruthenium is generally applied on the anode side, and platinum is applied on the cathode side. Catalysts may be optionally supported on carbon. The catalyst is initially dispersed in a small amount of water (about 100mg of catalyst in 1 g of water). To this dispersion a 5% ionomer solution in water/alcohol is added (0.25-0.75 g). The resulting dispersion may be directly painted onto the polymer membrane. Alternatively, isopropanol (1-3 g) is added and the dispersion is directly sprayed onto the membrane. The catalyst may also be applied onto the membrane by decal transfer, as described in the open literature (*Electrochimica Acta*, 40: 297 (1995)).

The CCM is used to make MEA's. As used herein, an MEA refers to an ion conducting polymer membrane made from a CCM according to the invention in combination with anode and cathode electrodes positioned to be in electrical contact with the catalyst layer of the CCM.

The electrodes are in electrical contact with the catalyst layer, either directly or indirectly, when they are capable of completing an electrical circuit which includes the CCM and a load to which the fuel cell current is supplied. More particularly, a first catalyst is electrocatalytically associated with the anode

side of the PEM so as to facilitate the oxidation of hydrogen or organic fuel. Such oxidation generally results in the formation of protons, electrons and, in the case of organic fuels, carbon dioxide and water. Since the membrane is substantially impermeable to molecular hydrogen and organic fuels such as methanol, as well as carbon dioxide, such components remain on the anodic side of the membrane. Electrons formed from the electrocatalytic reaction are transmitted from the cathode to the load and then to the anode. Balancing this direct electron current is the transfer of an equivalent number of protons across the membrane to the anodic compartment. There an electrocatalytic reduction of oxygen in the presence of the transmitted protons occurs to form water. In one embodiment, air is the source of oxygen. In another embodiment, oxygen-enriched air is used.

The membrane electrode assembly is generally used to divide a fuel cell into anodic and cathodic compartments. In such fuel cell systems, a fuel such as hydrogen gas or an organic fuel such as methanol is added to the anodic compartment while an oxidant such as oxygen or ambient air is allowed to enter the cathodic compartment. Depending upon the particular use of a fuel cell, a number of cells can be combined to achieve appropriate voltage and power output. Such applications include electrical power sources for residential, industrial, commercial power systems and for use in locomotive power such as in automobiles. Other uses to which the invention finds particular use includes the use of fuel cells in portable electronic devices such as cell phones and other telecommunication devices, video and audio consumer electronics equipment, computer laptops, computer notebooks, personal digital assistants and other computing devices, GPS devices and the like. In addition, the fuel cells may be stacked to increase voltage and current capacity for use in high power applications such as industrial and residential sewer services or used to provide locomotion to vehicles. Such fuel cell structures include those disclosed in U.S. Patent Nos. 6,416,895, 6,413,664, 6,106,964, 5,840,438, 5,773,160, 5,750,281, 5,547,776, 5,527,363, 5,521,018,



5,514,487, 5,482,680, 5,432,021, 5,382,478, 5,300,370, 5,252,410 and 5,230,966.

Such CCM and MEM's are generally useful in fuel cells such as those disclosed in U.S. Patent Nos. 5,945,231, 5,773,162, 5,992,008, 5,723,229, 5 6,057,051, 5,976,725, 5,789,093, 4,612,261, 4,407,905, 4,629,664, 4,562,123, 4,789,917, 4,446,210, 4,390,603, 6,110,613, 6,020,083, 5,480,735, 4,851,377, 4,420,544, 5,759,712, 5,807,412, 5,670,266, 5,916,699, 5,693,434, 5,688,613, 5,688,614, each of which is expressly incorporated herein by reference.

10 The CCM's and MEA's of the invention may also be used in hydrogen fuel cells which are known in the art.

The ion conducting polymer membranes of the invention also find use as separators in batteries. Particularly preferred batteries are lithium ion batteries.

### EXAMPLES

15 The following examples provide further support for the types of reactions and polymers described throughout this specification.

#### *Example 1 (JC58-42):*

Oligomer 1: DP = 4

20 This oligomer was synthesized in a similar way as described in oligomer 1, using following compositions: 4,4'-difluorobenzophone (BisK, 34.91 g, 0.16 mol), 9,9-bis(4-hydroxyphenyl)fluorene (42.05 g, 0.12 mol), and anhydrous potassium carbonate (25.87 g, 0.187 mol), 220 mL of DMSO and 110 mL of toluene.

25 This block polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 7.75 g, 0.0355 mol), 3,3'-disulfonated-4,4'-difluorobenzophone ((SBisK, 15.00 g, 0.0355 mol), Oligomer 1 (20.90 g), BisZ (21.47 g, 0.08 mol), and anhydrous

potassium carbonate (14.37 g, 0.10 mol), 250 mL of DMSO and 125 mL of toluene. This polymer has an inherent viscosity of 0.49 dl/g in DMAc (0.25 g/dl). Its one-day swelling in 8 M methanol at 80°C was 52%, cross-over in 8 M methanol was 0.016 mg.mil/cc.min.cm<sup>2</sup> (non-boiled, conductivity was 0.013 S/cm (non-boiled) and 0.034 S/cm (boiled).

*Example 2 (JC58-73):*

This block polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 5.72 g, 0.026 mol), 3,3'-disulfonated-4,4'-difluorobenzophone ((SBisK, 17.04 g, 0.040 mol), Oligomer 1 (19.59 g), BisZ (20.12 g, 0.075 mol), and anhydrous potassium carbonate (13.47 g, 0.097 mol), 250 mL of DMSO and 125 mL of Toluene. This polymer has an inherent viscosity of 0.72 dl/g in DMAc (0.25 g/dl).

*Example 3 (JC58-85):*

This block polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 4.68 g, 0.021 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SbisK, 19.06 g, 0.045 mol), Oligomer 1 (19.59 g), 9,9-bis(4-hydroxyphenyl)fluorine (26.28 g, 0.075 mol), and anhydrous potassium carbonate (13.47 g, 0.097 mol), 250 mL of DMSO and 125 mL of Toluene.

*Example 4(JC58-86):*

This block polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 4.68 g, 0.021 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 19.06 g, 0.040 mol), Oligomer 1 (19.59 g), bisphenol (13.96 g, 0.075 mol), and anhydrous potassium carbonate (13.47 g, 0.075 mol), 250 mL of DMSO and 125 mL of toluene.

*Example 5 (JC58-89):*

This block polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 4.68 g, 0.021 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 19.06 g, 0.040 mol), Oligomer 2 (19.59 g), 1,5-dihydroxynaphthalene (12.01 g, 0.075 mol),  
5 and anhydrous potassium carbonate (13.47 g, 0.097 mol), 250 mL of DMSO and 125 mL of toluene.

*Example 6 (JC58-69):*

This example illustrates block copolymer system using BisK-O block in the non-ionic region, and SBisK-Z in ionic region, the non-ionic region consists of  
10 11%. Size 6 of BisK-O block.

Oligomer 2: DP = 6

This oligomer was synthesized in a similar way as described in oligomer 1, using following compositions: 4,4'-difluorobenzophone (BisK, 65.46 g, 0.30 mol), 4,4'-dihydroxydiphenyl ether (0, 50.55 g, 0.25 mol), and anhydrous  
15 potassium carbonate (44.92 g, 0.325 mol), 540 mL of DMSO and 270 mL of toluene.

This block polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 6.51 g, 0.030 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 17.40 g, 0.041 mol),  
20 Oligomer 2 (22.40 g), BisZ (21.47 g, 0.08 mol), and anhydrous potassium carbonate (14.37 g, 0.10 mol), 250 mL of DMSO and 125 mL of toluene.

*Examples 7-13* illustrate block copolymer system using same BisK-Z in non-ionic region, but sBisK with various aryl phenol groups block having different chain mobility and chemical affinity in the ionic region. The non-ionic block  
25 size is 8 and block concentration is 11%.

*Example 7 illustrates ionic region consist of sBisK-Z unit (JC58-45):*

Oligomer 3: DP = 8

This oligomer was synthesized in a similar way as described in oligomer 1, using following compositions: 4,4'-difluorobenzophone (BisK, 65.46 g, 0.3 mol), BisZ (70.44 g, 0.262 mol), and anhydrous potassium carbonate (17.97 g, 0.13 mol), 540 mL of anhydrous DMSO (270 mL) of toluene. This block  
5 polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 4.57 g, 0.021 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisZ 17.41 g, 0.041 mol), Oligomer 3 (29.72 g), BisZ (18.78 g, 0.07 mol), and anhydrous potassium carbonate (12.57 g, 0.091 mol), 270 mL of anhydrous DMSO and 135 mL of  
10 toluene. This polymer has an inherent viscosity of 0.62 dl/g in DMAc (0.25 g/dl).

*Example 8 illustrates ionic region consist of sBisK-FL unit (JC58-44:)*

This block polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 3.91 g, 0.0179 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 14.92 g, 0.06  
15 mol), Oligomer 3 (25.27 g), 9,9-bis(4-hydroxyphenyl)fluorene (21.02 g, 0.07 mol), and anhydrous potassium carbonate (10.78 g, 0.078 mol), 250 mL of DMSO and 125 mL of toluene. This polymer has an inherent viscosity of 0.84 dl/g in DMAc (0.25 g/dl).

20 *Example 9 illustrates ionic region consist of sBisK-AF unit (JC58-66):*

This block polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 3.91 g, 0.0179 mol), 3,3'-disulfonated-4,4'-difluorobenzophone ((SBisK, 14.92 g, 0.035 mol), Oligomer 3 (25.47 g), 4,4'-(Hexafluoroisopropylidene)-diphenol  
25 (20.17 g, 0.06 mol), and anhydrous potassium carbonate (10.78 g, 0.078 mol), 250 mL of DMSO and 125 mL of toluene.

This polymer has an inherent viscosity of 0.47 dl/g in DMAc (0.25 g/dl).

*Example 10 illustrates ionic region consisting of sBisK-B unit (JC58-61)*

This block polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 4.57 g, 0.021 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 17.41 g, 0.041 mol), Oligomer 3 (29.72 g), 4,4'-dihydroxybiphenyl (13.03 g, 0.07 mol), and anhydrous potassium carbonate (12.57 g, 0.091 mol), 250 mL of DMSO and 125 mL of toluene. This polymer has an inherent viscosity of 1.01 dl/g in DMAc (0.25 g/dl).

*Example 11 illustrates ionic region consisting of sBisK-O unit (JC58-60)*

This block polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 4.57 g, 0.021 mol), 3,3'-disulfonated-4,4'-difluorobenzophone ((SBisK, 17.41 g, 0.041 mol), Oligomer 3 (29.72 g), 4,4'-dihydroxydiphenyl ether (14.15 g, 0.07 mol), and anhydrous potassium carbonate (12.57 g, 0.091 mol), 250 mL of DMSO and 125 mL of toluene. This polymer has an inherent viscosity of 0.94 dl/g in DMAc (0.25 g/dl).

*Example 12 (JC58-76):*

This block polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 1.298 g, 0.0059 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 23.736 g, 0.056 mol), Oligomer 3 (29.72 g), 4,4'-dihydroxydiphenyl (13.03 g, 0.07 mol), and anhydrous potassium carbonate (12.57 g, 0.091 mol), 250 mL of DMSO and 125 mL of toluene. This polymer has an inherent viscosity of 1.35 dl/g in DMAc (0.25 g/dl).

*Example 13 (JC58-74):*

This block polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 3.91 g, 0.018 mol), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 14.92 g, 0.035 mol), Oligomer 3 (25.47 g), 1,5-dihydroxynaphthalene (9.61 g, 0.060 mol),

and anhydrous potassium carbonate (10.71 g, 0.078 mol), 206 mL of DMSO and 103 mL of Toluene. This polymer has an inherent viscosity of 1.10 dl/g in DMAc (0.25 g/dl).

5 *Table 1* summarizes the impact of the chain length and flexible in the ionic region on the final membrane properties from Examples 10-16.

Polymer	One-day Swelling (%)	Cross-over in 8M Methanol (mg.mil/cc.min.cm <sup>2</sup> ) (Non-boiled/boiled)	Conductivity (S/cm) (Non-boiled/boiled)
Example 7	116	0.034/0.081	0.38/0.055
Example 8	46	0.025/0.020	0.026/0.045
Example 9	141	0.0320/0.11	0.025/0.35
Example 10	47	0.036	0.047/0.075
Example 11	155	0.038/0.11	0.059/0.058
Example 12	62	0.026/0.046	0.061/0.085
Example 13	94	0.056/0.098	0.10/0.11

*Example 14* illustrates block copolymer system using BisK-Z block in the non-ionic region, and multi components (more than 2 unit) in the ionic region, in comparison of random copolymer of multi components system.

10 *Example 14 (JC 58-50):*

This block polymer was synthesized in a similar way as described in example 1, using following compositions: 4,4'-difluorobenzophone (BisK, 3.91 g, 0.0179 mol), 3,3'-disulfonated-4,4'-difluorobenzophone ((SBisK, 14.92 g, 0.035 mol), Oligomer 3 (25.27 g), BisZ (8.05 g, 0.035 mol), 9,9-bis(4-hydroxyphenyl)fluorene (10.51 g, 0.035 mol), and anhydrous potassium carbonate (10.78 g, 0.078 mol), 250 mL of DMSO and 125 mL of toluene. This polymer has an inherent viscosity of 1.02 dl/g in DMAc (0.25 g/dl). Its

one-day swelling in 8 M methanol at 80°C was 63%, cross-over in 8 M methanol was 0.036 mg.mil/cc.min.cm<sup>2</sup> (non-boiled) and 0.038 mg.mil/cc.min.cm<sup>2</sup> (boiled), conductivity was 0.026 S/cm (non-boiled) and 0.047 S/cm (boiled).

5      *Example 15*

Oligomer 1 (FL4): DP = 4

10      In a 500 mL three necked round flask, equipped with a mechanical stirrer, a thermometer probe connected with a nitrogen inlet, and a Dean-Stark trap/condenser, 4,4'-difluorobenzophone (BisK, 34.91 g, 0.16 mol), 9,9-bis(4-hydroxyphenyl)fluorene (42.05 g, 0.12 mol), and anhydrous potassium carbonate (25.87 g, 0.187 mol), 220 mL of DMSO and 110 mL of Toluene. The reaction mixture was slowly stirred under a slow nitrogen stream. After heating at ~85 °C for 1h and at ~120 °C for 1 h, the reaction temperature was raised to ~135 °C for 3 h, and finally to ~170 °C for 2 h. After cooling to ~70 °C with continuing stirring, the solution was dropped into 1L of cooled methanol with a vigorous stirring. The precipitates were filtrated and washed with DI-water four times and dried at 80 °C overnight, and then dried at 80 °C under vacuum for 2 days.

BlkFL4FL/45 (JC58-85)

20      This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 4.68 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 19.06 g), Oligomer 1 (19.59 g), 9,9-bis(4-hydroxyphenyl)fluorene (26.28 g), and anhydrous potassium carbonate (13.48 g), 240 mL of DMSO and 120 mL of Toluene. This polymer has an inherent viscosity of 1.00 dl/g in DMAc (0.25 g/dl).

25      BlkFL4B/45 (JC58-86)

This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 4.68 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 19.06 g), Oligomer 1 (19.59 g), 4,4'-biphenol (13.97 g), and anhydrous potassium carbonate (13.48 g), 240 mL of DMSO and 120 mL of Toluene. This polymer has an inherent viscosity of 1.89 dl/g in DMAc (0.25 g/dl).

#### BlkFL4NAP/45 (JC58-89)

This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 4.68 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 19.06 g), Oligomer 1 (19.59 g), 2,7-dihydroxynaphthalene (12.01 g), and anhydrous potassium carbonate (13.48 g), 240 mL of DMSO and 120 mL of Toluene. This polymer has an inherent viscosity of 1.00 dl/g in DMAc (0.25 g/dl).

#### Example 16

Oligomer 2 (A8): DP = 8

This oligomer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 87.28 g), 4,4'-(1,4-phenylenediisopropylidene)biphenol (79.90 g), and anhydrous potassium carbonate (62.88 g), 560 mL of DMSO and 280 mL of Toluene.

#### BlkA8FL/33 (JC58-93)

This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 1.94 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 7.50 g), Oligomer 2 (11.66 g), 9,9-bis(4-hydroxyphenyl)fluorene (10.51 g), and



anhydrous potassium carbonate (5.39 g), 120 mL of DMSO and 60 mL of Toluene. This polymer has an inherent viscosity of 0.84 dl/g in DMAc (0.25 g/dl).

BlkA8B/33 (JC58-94)

5 This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 1.94 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 7.50 g), Oligomer 2 (11.66 g), 4,4'-biphenol (5.58 g), and anhydrous potassium carbonate (5.39 g), 120 mL of DMSO and 60 mL of Toluene. This polymer  
10 has an inherent viscosity of 1.12 dl/g in DMAc (0.25 g/dl).

BlkA8Z/33 (JC58-95)

This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 1.94 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 7.50 g),  
15 Oligomer 2 (11.66 g), 1,1-bis(4-hydroxyphenyl)cyclohexane (8.05 g), and anhydrous potassium carbonate (5.39 g), 120 mL of DMSO and 60 mL of Toluene. This polymer has an inherent viscosity of 0.64 dl/g in DMAc (0.25 g/dl).

BlkA8FL/45 (JC58-97)

20 This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 0.64 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 11.88 g), Oligomer 2 (13.60 g), 9,9-bis(4-hydroxyphenyl)fluorene (12.26 g), and anhydrous potassium carbonate (6.29 g), 150 mL of DMSO and 75 mL of  
25 Toluene. This polymer has an inherent viscosity of 0.68 dl/g in DMAc (0.25 g/dl).

BlkA8A/33 (JC58-103)

This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 1.94 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 7.50 g), Oligomer 2 (11.66 g), 4,4'-(1,4-phenylenediisopropylidene)bisphenol (6.85 g),  
5 and anhydrous potassium carbonate (5.39 g), 120 mL of DMSO and 60 mL of Toluene. This polymer has an inherent viscosity of 0.84 dl/g in DMAc (0.25 g/dl).

BlkA8NAP/33 (JC58-106)

*Example 17*

10 This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 2.42 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 9.37 g), Oligomer 2 (14.57 g), 2,7-dihydroxynaphthalene (6.00 g), and anhydrous potassium carbonate (6.74 g), 120 mL of DMSO and 60 mL of Toluene. This  
15 polymer has an inherent viscosity of 0.97 dl/g in DMAc (0.25 g/dl).

Oligomer 3 (AF8): DP = 8

This oligomer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 87.28 g), 4,4'-(hexafluoroisopropylidene)diphenol (117.69 g), and anhydrous  
20 potassium carbonate (62.88 g), 560 mL of DMSO and 280 mL of Toluene.

BlkAF8Z/33 (JC58-113)

This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 3.88 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 15.00 g),  
25 Oligomer 3 (29.12 g), 1,1-bis(4-hydroxyphenyl)cyclohexane (16.10 g), and anhydrous potassium carbonate (10.78 g), 240 mL of DMSO and 120 mL of Toluene. This polymer has an inherent viscosity of 0.72 dl/g in DMAc (0.25 g/dl).

## BlkAF8FL/33 (JC58-114)

This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 3.55 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 13.75 g),  
5 Oligomer 3 (26.70 g), 9,9-bis(4-hydroxyphenyl)fluorene (19.27 g), and anhydrous potassium carbonate (9.88 g), 240 mL of DMSO and 120 mL of Toluene. This polymer has an inherent viscosity of 0.50 dl/g in DMAc (0.25 g/dl).

## BlkAF8B/33 (JC58-115)

10 This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 4.20 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 16.25 g), Oligomer 3 (31.55 g), 4,4'-biphenol (12.10 g), and anhydrous potassium carbonate (11.68 g), 240 mL of DMSO and 120 mL of Toluene. This polymer  
15 has an inherent viscosity of 1.29 dl/g in DMAc (0.25 g/dl).

## BlkAF8AF/33 (JC58-140)

This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 3.55 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 13.75 g),  
20 Oligomer 3 (26.70 g), 4,4'-(hexafluoroisopropylidene)diphenol (18.49 g), and anhydrous potassium carbonate (9.88 g), 240 mL of DMSO and 120 mL of Toluene. This polymer has an inherent viscosity of 0.54 dl/g in DMAc (0.25 g/dl).

## BlkAF8NAP/33 (JC58-116)

25 This block polymer was synthesized in a similar way as described in the oligomer 1 synthesis, using following compositions: 4,4'-difluorobenzophone (BisK, 4.20 g), 3,3'-disulfonated-4,4'-difluorobenzophone (SBisK, 16.25 g), Oligomer 3 (31.55 g), 2,7-dihydroxynaphthalene (10.41 g), and anhydrous

potassium carbonate (11.68 g), 240 mL of DMSO and 120 mL of Toluene. This polymer has an inherent viscosity of 1.08 dl/g in DMAc (0.25 g/dl).

### *Example 18*

#### Synthesis of Oligomer with phenoxide end-groups

5 The typical synthesis procedure of phenoxide end-group oligomer with repeat unit number or degree of polymerization (DP) of 10 is presented here wherein DP is calculated from the formula  $DP=1/(1-p)$  where p is the molar fraction of the second component when the first component is equal to 1: In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer,  
10 nitrogen inlet and Dean-Stark trap/condenser, bisphenol A(9.128g), 4,4'-difluorobenzophenone (7.8552g) and anhydrous potassium carbonate (7.2g) were dissolved in a mixture of DMSO and toluene (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 150°C for 4h, then increasing the temperature to  
15 175-180°C for 6h. The reaction mixture was precipitated with acetone or methanol to get the crude product, then washed with hot water four times.

#### Synthesis of Oligomer with fluorine end-groups

The typical synthesis procedure of fluorine end-group oligomer with repeat unit number 10 is presented here. In a 500ml three necked round flask,  
20 equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, bisphenol A(8.2152g), sulfonated 4,4'-difluorobenzophenone (5.9108g), 4,4'-difluorobenzophenone (5.6732g) and anhydrous potassium carbonate (7.2g) were dissolved in a mixture of DMSO and Toluene (about 20% solid concentration). The mixture was heated to  
25 toluene reflux with stirring, keeping the temperature at 150°C for 4h, then increasing the temperature to 175-180°C for 6h. The reaction mixture was precipitated with acetone or methanol to get the crude product, then washed with hot water four times.

### Synthesis of Regular Block Copolymers

When the preparation of the fluorine-terminated oligomer was complete, the solution was cooled to 120°C, and introduced directly into a reaction flask containing the phenoxide-terminated oligomer under nitrogen atmosphere. To  
5 obtain the equivalent molar molar ration of a phenoxide end-groups and fluorine end-groups, the phenoxide-terminated oligomer reaction flask was washed three times with 20ml DMSO, and the solution was combined and also poured in the reaction flask. Then the temperature was again raised to 175-  
10 180°C, and maintained there for 6h. The reaction mixture was filtered and a solid precipitated from acetone or methanol to get the crude product, then washed by hot water four times.

Conductivity: 0.046S/cm, swelling by area in 8M methanol: 88%, 8M methanol cross-over:  $8.3 \times 10^{-7} \text{ cm}^2/\text{sec}$ .

#### *Example 19*

15 Synthesis of partial block polymer with non-sulfonated hydrophobic segment

Fluorine end group oligomer preparation (Segment size  $n=4$ )

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (80.508), Bis K(87.28g), anhydrous potassium carbonate (54g) were dissolved in a  
20 mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 4h, then increase temperature to 175°C for 4h. The oligomer precipitates from methanol to get the rude product, then washed by hot water four times. Dry at 80C oven for one day and 75C vacuum oven for 2 days.

25 Polymerization

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (13.418), Bis

K(4.8878g), S-Bis K(9.2884g), oligomer(11.2112g), anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture precipitates from methanol to get the crude product.

Conductivity: 0.015S/cm, Swelling by area in 8M methanol solution: 51%, 8M Methanol Cross-over:  $3.5 \times 10^{-7} \text{ cm}^2/\text{sec}$ .

#### *Example 20*

##### 10 *BPE-3 (BLKZ4Z-28)*

Synthesis of partial block polymer with non-sulfonated hydrophobic segment  
Fluorine end group oligomer (BisZ/BisK) preparation (segment size n=4)

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (80.508), Bis K(87.28g), anhydrous potassium carbonate (54g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 4h, then increase temperature to 175°C for 4h. The reaction mixture precipitates from methanol to get the crude product, and then washed by hot water four times. Dry at 80C oven for one day and 75C vacuum oven for 2days.

#### *Polymerization*

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (13.418), Bis K(5.2368g), S-Bis K(8.4444g), oligomer(12.0112g, n=4, fluorine end of BisZ/BisK composition), anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration).

The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture precipitates from methanol to get the rude product.

5 Conductivity: 0.014S/cm (0.038 S/cm, boiled), swelling by area in 8M methanol: 60%, 8M methanol cross-over: 0.019 mg/min.ml.mls.

*Example 21*

BPE-5 (BLKZ4Z-33)

10 In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (13.418), Bis K(4.8878g), S-Bis K(9.2884g), oligomer(11.2112g, n=4, fluorine end of BisZ/BisK composition), anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The  
15 reaction mixture precipitates from methanol to get the rude product.

Conductivity: 0.0146S/cm (0.0378 S/cm, boiled), swelling by area in 8M methanol: 51%, 8M methanol cross-over: 0.022 mg/min.ml.mls.

*Example 22*

## BPE-1(BLKZ6Z-30)

Synthesis of partial block polymer with non-sulfonated hydrophobic segment

Fluorine end group oligomer preparation (segment size  $n=6$ )

- 5 In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (89.4533g), 4,4'-difluorobenzophone (Bis K, 87.28g), anhydrous potassium carbonate (54g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping
- 10 the temperature at 140°C for 4h, then increase temperature to 175°C for 4h. The reaction mixture precipitates from methanol to get the rude product, and then washed by hot water four times. Dry at 80C oven for one day and 75C vacuum oven for 2days.

Polymerization

- 15 In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (13.418), Bis K(4.8878g), 3,3'-disulfonated-4,4'-difluorobenzophone (S-Bis K, 8.444g), oligomer(9.953g,  $n=6$ , fluorine end of BisZ/BisK composition), anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene
- 20 (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture precipitates from methanol to get the rude product.



*Example 23*

## BLKZ4B-30

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-Biphenol  
5 (9.3105), Bis K(4.8878g), S-Bis K(9.2884g), oligomer(11.2112g, n=4, fluorine end of BisZ/BisK composition), anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-  
10 4.5h. The reaction mixture precipitates from methanol to get the rude product.

Conductivity: 0.012S/cm(0.0211 S/cm, boiled), swelling by area in 8M methanol: 21%,

*Example 24*

## BLKZ4B-34

15 In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-Biphenol (8.3794g), Bis K(1.2444g), S-Bis K(12.9794g), oligomer(18.00g, n=4, fluorine end of BisZ/BisK composition), anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene (about 20% solid  
20 concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture precipitates from methanol to get the rude product.

Conductivity: 0.0427S/cm(0.078S/cm, boiled), swelling by area in 8M methanol: 61%, 8M methanol cross-over: 0.052 mg/min.ml.mls.

*Example 25*

## BLKZ4B-36

5 In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-Biphenol (8.3794g), Bis K(1.1032g), S-Bis K(13.6625g), oligomer(15.1777g, n=4, fluorine end of BisZ/BisK composition), anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture precipitates from methanol to get the rude product.

10 Conductivity: 0.067S/cm(0.096 S/cm, boiled), swelling by area in 8M methanol: 72%, 8M methanol cross-over: 0.06 mg/min.ml.mls.

*Example 26*

BLKZ4B-40

15 In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-Biphenol (8.3794), Bis K(0.3078g), S-Bis K(15.0287g), oligomer(16.0714g, n=4, fluorine end of BisZ/BisK composition), anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture precipitates from methanol to get the rude product.

20 Conductivity: 0.072S/cm(0.0922 S/cm, boiled), swelling by area in 8M methanol: 98%, 8M methanol cross-over: 0.067 mg/min.ml.mls.

*Example 27*

BLKZ4F-30

25 In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-(Hexafluoroisopropylidene)-diphenol (6F, 16.8065g), Bis K(4.8878g), S-Bis

K(9.2884g), oligomer(11.2112g, n=4, fluorine end of BisZ/BisK composition), anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture precipitates from methanol to get the rude product.

Conductivity: 0.007S/cm(0.0122 S/cm, boiled), swelling by area in 8M methanol: 24%, 8M methanol cross-over: 0.016 mg/min.ml.mls.

#### *Example 28*

BLKF4Z-30

Synthesis of partial block polymer with non-sulfonated hydrophobic segment

Fluorine end group oligomer(6F/BisK) preparation (segment size n=4)

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-(Hexafluoroisopropylidene)-diphenol (6F, 100.839g), Bis K(87.28g), anhydrous potassium carbonate (54g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 4h, then increase temperature to 175°C for 4h. The reaction mixture precipitates from methanol to get the rude product, and then washed by hot water four times. Dry at 80C oven for one day and 75C vacuum oven for 2days

#### Polymerization

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (13.418), Bis K(4.8878g), S-Bis K(9.2884g), oligomer(12.7333g, n=4, fluorine end of 6F/BisK composition), anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The

mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture precipitates from methanol to get the rude product.

5 Conductivity: 0.0114S/cm(0.0321 S/cm, boiled), swelling by area in 8M methanol: 38%, 8M methanol cross-over: 0.013 mg/min.ml.mls.

*Example 29*

BLKF4P-30

10 In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-(1,4-phenyldiisopropylidene)bisphenol (17.30g), Bis K(4.8878g), S-Bis K(9.2884g), oligomer(12.733g, n=4, fluorine end of 6F/BisK composition), anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase  
15 temperature to 173-175°C for 4-4.5h. The reaction mixture precipitates from methanol to get the rude product.

Conductivity: 0.0102S/cm(0.0215 S/cm, boiled), swelling by area in 8M methanol: 37%

*Example 30*

20 BLKF8Z-30

Synthesis of partial block polymer with non-sulfonated hydrophobic segment

Fluorine end group oligomer(6F/BisK) preparation (segment size n=8)

In a 500ml three necked round flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet and Dean-Stark trap/condenser, 4,4'-

25

(Hexafluoroisopropylidene)-diphenol (6F, 117.6455g), Bis K(87.28g), anhydrous potassium carbonate (54g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 4h, then increase  
5 temperature to 175°C for 4h. The reaction mixture precipitates from methanol to get the rude product, and then washed by hot water four times. Dry at 80C oven for one day and 75C vacuum oven for 2days

### Polymerization

In a 500ml three necked round flask, equipped with a mechanical stirrer,  
10 thermometer, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (13.418), Bis K(3.2729g), S-Bis K(12.4151g), oligomer(24.2454g, n=8, fluorine end of 6F/BisK composition), anhydrous potassium carbonate (9.0g) were dissolved in a mixture DMSO and Toluene (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at  
15 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture precipitates from methanol to get the rude product.

Conductivity: 0.011S/cm(0.0211S/cm, boiled), swelling by area in 8M methanol: 37%, 8M methanol cross-over: 0.023 mg/min.ml.mls.

### Example 31

20 Following examples demonstrate the effect of various block size and sulfonation degree

#### Oligomer Preparation (Block size n = 4)

Reference 37-119

In a 2L three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark  
25 trap/condenser, Bis Z (80.508), Bis K(87.28g), anhydrous potassium carbonate (71.86g) were dissolved in a mixture DMSO and toluene, 720 ml and 360 ml respectively (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 140°C for 4h, then

increasing the temperature to 175°C for 4h. The reaction mixture was precipitated into 2 L of methanol to get the crude product; then washed with hot DI water four times. The product was oven dried at 80C for one day and vacuum dried at 75C for 2 days.

5            Polymerization            BLKZ4/33            Reference 37-123

In a 500ml three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (13.418), Bis K(4.8878g), S-Bis K sodium salt (9.2902g), oligomer (n = 4 – Reference 37-119) (11.2112g), anhydrous  
 10            potassium carbonate (17.9g) were dissolved in a mixture dimethylsulfoxide (DMSO) (180 ml) and toluene (90 ml) (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture was precipitated into 2 L of methanol. The polymer was then washed  
 15            with DI water 4 times. The product was oven dried at 80C for one day and vacuum dried at 75C for 2 days. The dried sample (0.1250g) was in 25 ml of dimethylacetamide (DMAc) to determine inherent viscosity. The inherent viscosity of the sodium salt polymer was found to be 0.67 dL/g. A sample was prepared for GPC analysis by dissolving 50 mg of polymer in 20 ml of DMAc  
 20            containing 0.1M LiBr. The sample was found to have a peak molecular weight of about 46, 350 based upon polystyrene standards.

Polymerization            BLKZ4/25            Reference 37-124

In a 500ml three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark  
 25            trap/condenser, Bis Z (13.418), Bis K(6.0441g), S-Bis K sodium salt (7.0521g), oligomer (n = 4 – Reference 37-119) (17.2480g), anhydrous potassium carbonate (17.9g) were dissolved in a mixture dimethylsulfoxide (DMSO) (180 ml) and toluene (90 ml) (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at

140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture was precipitated into 2 L of methanol. The polymer was then washed with DI water 4 times. The product was oven dried at 80C for one day and vacuum dried at 75C for 2 days. The dried sample (0.1250g) was in 25 ml of dimethylacetamide (DMAc) to determine inherent viscosity. The inherent viscosity of the sodium salt polymer was found to be 0.49 dL/g.

Polymerization                      BLKZ4/40                      Reference 37-125

In a 500ml three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (13.418g), Bis K(3.8621g), S-Bis K sodium salt (11.2750g), oligomer (n = 4 – Reference 37-119) (17.2481g), anhydrous potassium carbonate (17.9g) were dissolved in a mixture dimethylsulfoxide (DMSO) (180 ml) and toluene (90 ml) (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture was precipitated into 2 L of methanol. The polymer was then washed with DI water 4 times. The product was oven dried at 80C for one day and vacuum dried at 75C for 2 days. The dried sample (0.1250g) was in 25 ml of dimethylacetamide (DMAc) to determine inherent viscosity. The inherent viscosity of the sodium salt polymer was found to be 0.643 dL/g.

Oligomer Preparation (Block size n = 8)                      Reference 37-152

In a 2L three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (70.4445g), Bis K(65.4600g), anhydrous potassium carbonate (47.1912g) were dissolved in a mixture DMSO and toluene, 540 ml and 270 ml respectively (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 140°C for 4h, then increasing the temperature to 175°C for 4h. The reaction mixture was

precipitated into 2 L of methanol to get the crude product; then washed with hot DI water four times. The product was oven dried at 80C for one day and vacuum dried at 75C for 2 days.

Polymerization

BLKZ8/33

Reference 37-134

5 In a 500ml three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (13.4180g), Bis K(3.2729g), S-Bis K sodium salt (12.4151g), oligomer (n = 8) (21.2299g), anhydrous potassium carbonate (17.9g) were dissolved in a mixture dimethylsulfoxide (DMSO) (180 ml) and  
10 toluene (90 ml) (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture was precipitated into 2 L of methanol. The polymer was then washed with DI water 4 times. The product was oven dried at 80C for one day and vacuum  
15 dried at 75C for 2 days. The dried sample (0.1250g) was in 25 ml of dimethylacetamide (DMAc) to determine inherent viscosity. The inherent viscosity of the sodium salt polymer was found to be 0.90 dL/g.

Polymerization

BLKZ8/25

Reference 37-132

20 In a 500ml three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (13.4180g), Bis K(4.8223g), S-Bis K sodium salt (9.4169g), oligomer (n = 8) (21.2296g), anhydrous potassium carbonate (17.9g) were dissolved in a mixture dimethylsulfoxide (DMSO) (180 ml) and toluene (90 ml) (about 20% solid concentration). The mixture was heated to  
25 toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture was precipitated into 2 L of methanol. The polymer was then washed with DI water 4 times. The product was oven dried at 80C for one day and vacuum



dried at 75C for 2 days. The dried sample (0.1250g) was in 25 ml of dimethylacetamide (DMAc) to determine inherent viscosity. The inherent viscosity of the sodium salt polymer was found to be 0.935 dL/g. A sample was prepared for GPC analysis by dissolving 50 mg of polymer in 20 ml of DMAc containing 0.1M LiBr. The sample was found to have a peak molecular weight of about 106,040 based upon polystyrene standards.

Polymerization                      BLKZ8/40                      Reference 37-128

In a 500ml three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (13.4180g), Bis K(1.8984g), S-Bis K sodium salt (15.0757g), oligomer (n = 8) (21.2296g), anhydrous potassium carbonate (17.9g) were dissolved in a mixture dimethylsulfoxide (DMSO) (180 ml) and toluene (90 ml) (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture was precipitated into 2 L of methanol. The polymer was then washed with DI water 4 times. The product was oven dried at 80C for one day and vacuum dried at 75C for 2 days. The dried sample (0.1250g) was in 25 ml of dimethylacetamide (DMAc) to determine inherent viscosity. The inherent viscosity of the sodium salt polymer was found to be 0.992 dL/g.

Oligomer Preparation (Block size n = 2)                      Reference 37-121

In a 2L three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (53.6721g), Bis K(87.2800g), anhydrous potassium carbonate (71.8692g) were dissolved in a mixture DMSO and toluene, 750 ml and 360 ml respectively (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 140°C for 4h, then increasing the temperature to 175°C for 4h. The reaction mixture was

precipitated into 2 L of methanol to get the crude product; then washed with hot DI water four times. The product was oven dried at 80C for one day and vacuum dried at 75C for 2 days.

Polymerization

BLKZ82/33

Reference 37-140

5 In a 500ml three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (20.1270g), Bis K(8.5424g), S-Bis K sodium salt (11.5917g), oligomer ( $n = 2$ ) (6.2215), anhydrous potassium carbonate (17.9g) were dissolved in a mixture dimethylsulfoxide (DMSO) (190 ml) and toluene 10 (100 ml) (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture was precipitated into 2 L of methanol. The polymer was then washed with DI water 4 times. 15 The product was oven dried at 80C for one day and vacuum dried at 75C for 2 days. The dried sample (0.1250g) was in 25 ml of dimethylacetamide (DMAc) to determine inherent viscosity. The inherent viscosity of the sodium salt polymer was found to be 0.466 dL/g.

Polymerization

BLKZ2/25

Reference 37-139

20 In a 500ml three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (20.1270g), Bis K(9.9827g), S-Bis K sodium salt (8.8046g), oligomer ( $n = 2$ ) (6.2214g), anhydrous potassium carbonate (27.0629g) were dissolved in a mixture dimethylsulfoxide (DMSO) (180 ml) and toluene (90 ml) (about 20% solid concentration). The mixture was heated 25 to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture was precipitated into 2 L of methanol. The polymer was then washed with DI water 4 times. The product was oven dried at 80C for one day and vacuum dried at 75C for 2 days.

## Polymerization

BLKZ2/40

Reference 37-137

5 In a 500ml three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (20.1270g), Bis K(7.2661), S-Bis K sodium salt (14.0620g), oligomer (n = 2) (6.2217g), anhydrous potassium carbonate (13.4759g) were dissolved in a mixture dimethylsulfoxide (DMSO) (180 ml) and toluene (90 ml) (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture was precipitated into 2 L of methanol. The polymer was then washed with DI water 4 times.

## Oligomer Preparation (Block size n = 12)

Reference 37-129

15 In a 1L three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (73.7990g), Bis K(65.4600g), anhydrous potassium carbonate (53.9019g) were dissolved in a mixture DMSO and toluene, 540 ml and 270 ml respectively (about 20% solid concentration). The mixture was heated to toluene reflux with stirring, keeping the temperature at 140°C for 4h, then increasing the temperature to 175°C for 4h. The reaction mixture was precipitated into 2 L of methanol to get the crude product; then washed with hot DI water four times. The product was oven dried at 80C for one day and vacuum dried at 75C for 2 days.

## Polymerization

BLKZ12/40

Reference 37-143

In a 500ml three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (20.1270g), S-Bis K sodium salt (28.1240g), oligomer (n = 12) (31.2316g), anhydrous potassium carbonate (13.5589g) were dissolved in a mixture dimethylsulfoxide (DMSO) (300 ml) and toluene (100 ml) (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture was precipitated into 2 L of methanol. The polymer was then washed with DI water 4 times. The dried sample (0.1250g) was in 25 ml of dimethylacetamide (DMAc) to determine inherent viscosity. The inherent viscosity of the sodium salt polymer was found to be 0.490 dL/g.

Polymerization                      BLKZ8/40-5.6                      Reference 37-156

In a 500ml three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (16.1017g), Bis K (6.3366g), S-Bis K sodium salt (11.6552g), oligomer (n = 8) (12.7379g), anhydrous potassium carbonate (10.7841g) were dissolved in a mixture dimethylsulfoxide (DMSO) (200 ml) and toluene (100 ml) (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture was precipitated into 2 L of methanol. The polymer was then washed with DI water 4 times. The polymer was found to have an inherent viscosity of 0.66 dL/g in the proton form.

Polymerization                      BLKZ8/33-16.8                      Reference 37-160

In a 500ml three necked round bottom flask, equipped with a mechanical stirrer, thermocouple, heating mantle, controller, nitrogen inlet and Dean-Stark trap/condenser, Bis Z (13.4180 g), S-Bis K sodium salt (17.5670 g), oligomer (n = 8) (31.8444 g), anhydrous potassium carbonate (8.9837 g) were dissolved

5 in a mixture dimethylsulfoxide (DMSO) (250 ml) and toluene (125 ml) (about 20% solid concentration). The mixture was heated to toluene flux with stirring, keeping the temperature at 140°C for 6h, then increase temperature to 173-175°C for 4-4.5h. The reaction mixture was precipitated into 2 L of methanol. The polymer was then washed with DI water 4 times. The polymer was found to have an inherent viscosity of 0.83 dL/g in the proton form.

All references cited throughout the specification, including those in the background, are specifically incorporated herein by reference in their entirety.

10 Although the present invention has been described with reference to preferred embodiments, persons skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

## CLAIMS

1. An ion conductive block copolymer composition comprising non-ionic and ionic regions having the formula



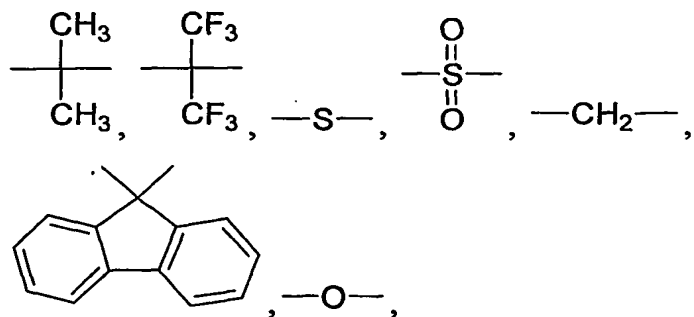
5  $[-(A_aB_b)_n]_{1-z}$  comprises a non-ionic polymer, and

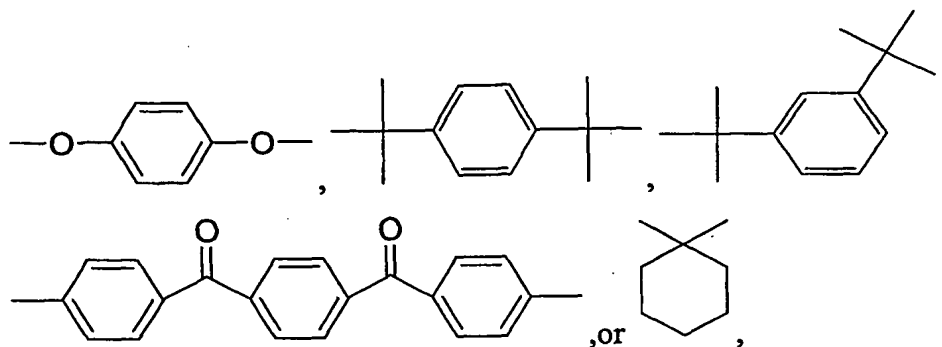
$[-(S_xC_c-S_yD_d)_o]_z$  comprises an ionic polymer, and wherein

at least one of said non-ionic or ionic polymers comprises a block within said ion conducting copolymer;

10 A and C are phenyl, naphthyl, terphenyl, aryl nitrile, substituted aryl nitrile, organopolysiloxane--Ar<sub>1</sub>—R<sub>1</sub>—Ar<sub>2</sub>--, where R<sub>1</sub> is, —C(O)—, —S(O)<sub>2</sub>—, —P(O)(C<sub>6</sub>H<sub>5</sub>)—, —C(O)—Ar<sub>3</sub>—C(O)—, or —C(O)—Ar<sub>4</sub>—S(O)<sub>2</sub>—, and Ar<sub>1</sub>, Ar<sub>2</sub>, Ar<sub>3</sub>, and Ar<sub>4</sub> are aromatic groups or substituted aromatic groups and wherein each A and C can be the same or different;

15 B and D are --O—Ar<sub>5</sub>—R<sub>2</sub>—Ar<sub>6</sub>—O--, where R<sub>2</sub> is a single bond, a cycloaliphatic of the formula C<sub>n</sub>H<sub>2n-2</sub>,





and  $Ar_5$  and  $Ar_6$  are aromatic groups or substituted aromatic groups and wherein each B and D can be the same or different;

- 5 S is an ion conducting group selected from the group  $-SO_3H$ ,  $-COOH$ ,  $-PO_3H$ , and  $SO_2NH_2SO_2R_f$ , where  $R_f$  is a polyfluorinated hydrocarbon having 1-20 carbon atoms; wherein S may be the same or different when more than one S is present;

n is an integer between 1 and 100;

- 10 o is an integer between 1 and 100;

a and b are integers each between 1 and n, where a indicates the number of different A and b the number of different B present in the non-ionic polymer  $(A_aB_b)_n$ ;

- 15 c and d are integers between 1 and o, where c indicates the number of different C and d the number of different D present in the ionic polymer  $(S_xC_c-S_yD_d)_o$ ;

x and y are respectively the percentage of C and D which contain S, wherein at least one of x or y is greater than 0%;

z is o divided by the sum of n and o and has a range from 0.001 to 1.0;

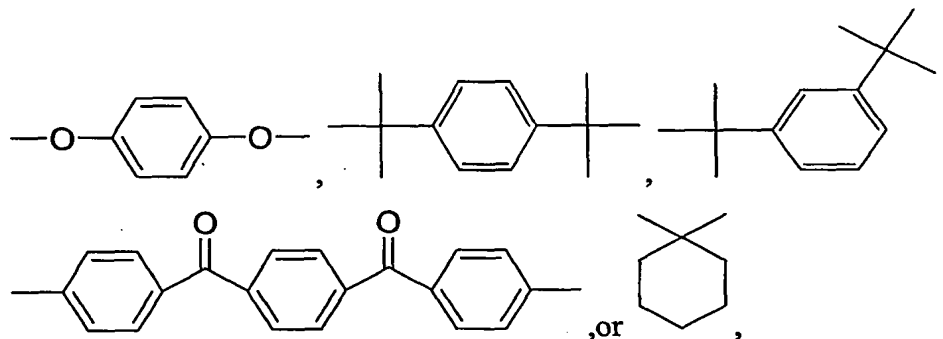
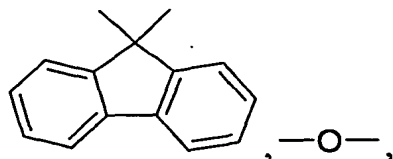
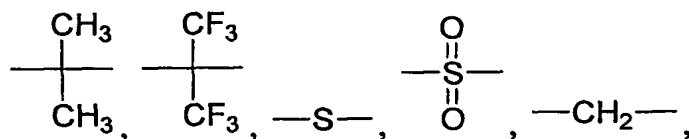
- 20 j is an integer between 1 and 200 and  $L_1$  is a bond or an additional B,  $L_2$  is a bond or an additional A and/or D, and  $L_3$  is a bond or an additional D.

2. The ion conductive polymer of claim 1 wherein S is randomly distributed within said ionic polymer.
3. The ion conductive polymer of claim 1 wherein S is in predetermined positions within said ionic polymer.
4. The ion conductive polymer of claim 1 wherein said ionic and non-ionic polymers comprise blocks in said ion conductive polymer.
5. The ion conductive polymer of claim 1 wherein o is between 2 and 20, and A and C are  $\text{Ar}_1\text{-C(O)-Ar}_2$ , B and D are same or different of cyclohexyldyl or fluorenyl, S is  $\text{SO}_3\text{H}$ , x+y is between 20 and 40%, z is between 0.2 and 0.5 and j is an integer between 60 and 150.
6. An ion conductive block copolymer composition comprising non-ionic and ionic regions having the formula
- $$\{[-\text{L}_1-(\text{A}_a\text{B}_b)_n-\text{L}_1-(\text{A}_e\text{B}_f)_m]_{1-z}-\text{L}_2-[(\text{S}_{x1}\text{C}_c-\text{S}_{y1}\text{D}_d)_o-\text{L}_3-(\text{S}_{x2}\text{C}_g-\text{S}_{y2}\text{D}_h)_p-\text{L}_3-]_z\}_j$$
- wherein
- $[-(\text{A}_a\text{B}_b)_n-(\text{A}_e\text{B}_f)_m]_{1-z}$  comprises a non-ionic polymer, and
- $[-(\text{S}_{x1}\text{C}_c-\text{S}_{y1}\text{D}_d)_o-(\text{S}_{x2}\text{C}_g-\text{S}_{y2}\text{D}_h)_p-]_z$  comprises an ionic polymer, and wherein
- at least one of  $(\text{A}_a\text{B}_b)_n$  or  $(\text{S}_{x1}\text{C}_c-\text{S}_{y1}\text{D}_d)_o$  are polymers comprising a block within said ion conducting polymer and  $(\text{A}_e\text{B}_f)_m$  and  $-(\text{S}_{x2}\text{C}_g-\text{S}_{y2}\text{D}_h)_p$  are polymers which are random in length composition or both;



A and C are phenyl, naphthyl, terphenyl, aryl nitrile, substituted aryl nitrile, organopolysiloxane--Ar<sub>1</sub>—R<sub>1</sub>—Ar<sub>2</sub>--, where R<sub>1</sub> is, —C(O)—, —S(O)<sub>2</sub>—, —P(O)(C<sub>6</sub>H<sub>5</sub>)—, —C(O)—Ar<sub>3</sub>—C(O)—, or —C(O)—Ar<sub>4</sub>—S(O)<sub>2</sub>—, and Ar<sub>1</sub>, Ar<sub>2</sub>, Ar<sub>3</sub>, and Ar<sub>4</sub> are aromatic groups of substituted aromatic groups wherein each A and C can be the same or different;

B and D are --O—Ar<sub>5</sub>—R<sub>2</sub>—Ar<sub>6</sub>—O-- , where R<sub>2</sub> is a single bond, a cycloaliphatic of the formula C<sub>n</sub>H<sub>2n-2</sub>,



and Ar<sub>5</sub> and Ar<sub>6</sub> are aromatic groups or substituted aromatic groups, wherein each B and D can be the same or different;

S is an acidic or basic group covalently attached to C and/or D selected from the group —SO<sub>3</sub>H, —COOH, —PO<sub>3</sub>H, and SO<sub>2</sub>NH<sub>2</sub>SO<sub>2</sub>R<sub>f</sub>, where R<sub>f</sub> is a polyfluorinated aliphatic having 1-20 carbon atoms; wherein S may be the same or different when more than one S is present;

n is an integer between 1 and 200;

m is an integer between 1 and 200;

a and b are integers each between 1 and n, where a indicates the number of different A and b the number of different B present in the non-ionic polymer  $(A_aB_b)_n$ ;

5 c and d are integers between 1 and 0, where c indicates the number of different C and d the number of different D present in the hydrophilic polymer  $(S_xC_c-S_yD_d)_o$ ;

e and f are integers each between 0 and m, where e indicates the number of different C and f the number of different D present in the ionic polymer  $(A_eB_f)_m$ ;

10 g and h are integers between 0 and p, where g indicates the number of different C and h the number of different D present in the ionic polymer  $(S_xC_g-S_yD_h)_p$ ;

$X_1$  and  $Y_1$  are respectively the percentage of  $C_c$  and  $D_d$  which contain S,  $X_2$  and  $Y_2$  are preferably the percentage of  $C_g$  and  $D_h$  which contains S wherein at least one of  $X_1$ ,  $X_2$ ,  $Y_1$  or  $Y_2$  is greater than 0%;

15

z is o plus p divided by the sum of m, n, o and p, where z has a range of from 0.001 to 1.0;

j is an integer between 1 and 200;

each  $L_1$  is independently a bond or an additional A and/or B;

20 each  $L_2$  is independently a bond or an additional A and/or D; and

each  $L_3$  is independently a bond or an additional C and/or D.

m is between 0 and 100 and p is between 0- and 100.

7. The ion conductive copolymer of claim 6 wherein  $(A_aB_b)_n$  and  $(S_{x1}C_c-S_{y1}D_d)$  comprise blocks within said ion conductive block copolymer.

25

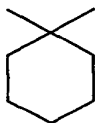
8. The ion conducting polymer of claim 6 wherein the ion conducting groups S are randomly distributed in the ionic polymer.

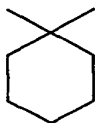
5 9. The ion conductive polymer of claim 6 wherein the ion conducting groups S are located in a predetermined position within said ionic polymer.

10. The ion conductive polymer of claim 6 wherein m and p are random numbers.

10

11. The ion conductive polymer composition of claim 5 wherein O is between 2 and 20, N is between 2 and 20, A and C are  $\text{Ar}_1\text{-C(O)-Ar}_2$ , B and D



are , S is  $\text{SO}_3\text{H}$ ,  $x+y$  is between 20 and 40%,  $z$  is between 0.2 and 0.5 and  $j$  is an integer between 60 and 150.

15

12. A polymer electrolyte membrane comprising the ion conducting block copolymer of claim 1 or 6.

20 13. A catalyst coated membrane comprising the membrane of claim 12 wherein all or part of at least one of the opposing surfaces of said membrane comprises a catalyst layer.

14. A membrane electrode assembly (MEA) comprising the catalyst coated membrane of claim 13 and electrodes in electrical contact with said catalyst layer.

5 15. A fuel cell comprising the membrane electrode assembly of claim 14.

16. An electronic device, system or motor comprising the fuel cell of claim 15.

10 17. A method for the preparation of a polymer electrolyte membrane (PEM) comprising the steps of

combining a first comonomer having at least two leaving groups and a second comonomer having at least two displacing groups, wherein said second comonomer is in excess relative to said first comonomer, thereby forming a  
15 first copolymer having displacing groups on the end of said first copolymer;

combining a third comonomer having at least two leaving groups and a fourth comonomer having at least two displacing groups, wherein said third comonomer is in excess relative to said fourth comonomer, thereby forming a second copolymer having leaving groups on the end of said second  
20 copolymer;

combining said first copolymer with said second copolymer, thereby forming a block copolymer, wherein at least one of said comonomers comprises an ionic group, and

forming said PEM from said block copolymer.

25

18. A method for making a catalyst coated membrane (CCM) comprising coating at least one surface of the PEM made according to claim 17 with a catalyst layer.

5 19. The PEM made according to claim 17.

20. The CCM made according to claim 18.

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(54) Title: ION CONDUCTIVE BLOCK COPOLYMERS

(57) Abstract: This invention relates to ion conductive copolymers which are useful in forming polymer electrolyte membranes used in fuel cells.

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# INTERNATIONAL SEARCH REPORT

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## A. CLASSIFICATION OF SUBJECT MATTER

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US CL : 429/30, 33, 314; 204/296; 521/27

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/30, 33, 314; 204/296; 521/27

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,214,488 B1 (HELMER-METZMANN et al ) 10 April 2001 (10.04.2001), col. 3, lines 33-64; col. 4, lines 1-6, 13-30; col. 7, lines 46-51; col. 8, lines 47-55 and col. 13, lines 29-50.	1-20

☐ Further documents are listed in the continuation of Box C.

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